THEORETICAL STUDIES OF IMPORTANT PROCESSES IN PLANETARY AND COMET ATMOSPHERES

Final Report

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A. Progress Under NASA Grant NAGW 1404

Dissociative recombination (DR) of molecular ions with electrons plays an integral role in determining the chemistry, ion and electron densities, temperature, spectral characteristics, and escape rates of planetary and comet atmospheres. For a diatomic or polyatomic ion, AB^+, DR is described by $AB^+ + e^- \rightarrow A + B$, where e^- is an electron and A and B are neutral fragments. Under NASA support we have completed the calculation of the DR cross sections and rates of OH^+ [Guberman, 1995a]. A reprint describing the calculations is attached in the Appendix. DR of OH^+ occurs in comets [Huebner, 1985] and may occur in the plasma torus of Saturn [Richardson, 1986]. However, the contribution of DR of OH^+ to comet and planetary models has been difficult to assess accurately since the rate of DR has never been measured directly in the laboratory or calculated theoretically prior to the work reported here. In addition, there was no information describing the state of the product O atom. The only prior work was a merged beam measurement [Mul et al., 1983] of the DR cross section which was not able to determine the state of excitation of the recombining ion. The range of electron energies covered by the experiment did not allow for the derivation of an accurate rate constant. As a result, the measured cross section and the approximate rate derived from it was not relevant to comet and planetary atmospheres.

In the ab initio calculations we used state of the art wave functions. The wave functions were described with large Gaussian basis sets including g basis functions. Large scale configuration interaction (CI) wave functions were generated for both the ion and the states that were possible dissociative routes. The highly accurate calculated spectroscopic constants are described in the Appendix. Five candidate dissociative routes were explored in the large scale calculations. We found that the only state that crossed the ion through the v=0 level was $2^2\Pi$. The CI wave function for this state had almost 900,000 configurations. It took 45 minutes to solve for the lowest two roots of $^2\Pi$ symmetry at each of 33 internuclear distances on a Cray YMP supercomputer. The electron capture widths were calculated using large Rydberg basis sets. For the electron angular momentum, ℓ, widths were calculated for both ℓ=1 and ℓ=2. The ℓ=2 width

was found to be negligibly small and only the ℓ=1 width was used. Because of the small calculated widths we found that the indirect DR mechanism plays only a small role. The calculated rate is small, 6.3 x 10^{-9} x $(T_e/300)^{-.48}$cm^3/sec for 10<T_e<1000K. Every recombination will lead to a hot H atom with 6.1 eV kinetic energy and a hot O(^{1}D) atom with 0.4eV kinetic energy. These are sufficient energies to allow for escape from comet atmospheres [Huebner, 1990]. In addition, each recombination will lead to production of the red line of O at 6300Å. Work has also started on a study of the effects of interloper states on the DR cross section and rate. The interloper states are Rydberg states with excited ion cores. These states can act as intermediates in DR.

We have also continued our calculations on the DR of O_2^+. A manuscript describing these calculations is in preparation [Guberman, 1995b]. Cross sections and rates have been calculated for DR along the $^1\Delta_u$ state of O_2. Dissociation along this route leads to two excited ^{1}D atoms. The cross sections have been calculated using Multichannel Quantum Defect Theory [Guberman and Giusti-Suzor, 1991]. The calculations included 25 vibrational levels for the ion and the Rydberg states. These calculations are an update to our prior calculations of DR [Guberman, 1988] which did not include the intermediate Rydberg resonance states. The latter states are neutral vibrationally excited states which lie above the v=0 level of the ion. These states are intermediate states in DR and lead to pronounced structure in the DR cross section. The resonances have an enormous effect near threshold. The full cross section is about 3 orders of magnitude below the direct cross section. Taking n to be the principal quantum number of the Rydberg level, the effect is primarily due to the n=3, v=13 Rydberg level which is centered at about 0.018eV below the threshold. This level has a wing which interferes destructively with direct recombination above threshold. The full calculated rate constant at 300K is 1.9 x 10^{-8} cm^3/sec and is a factor of 3.4 below the direct rate. The rate increases with temperature above 300K and reaches a maximum at 560K of 2.3 x 10^{-8} cm^3 /sec. Rates have been calculated for each of the lowest 10 vibrational levels.

In work supported by grant NAGW-1404, we have found that in addition to the $^1\Delta_u$ route, there are five other dissociative routes that are important for DR of the lowest 10 vibrational levels of O_2^+: $1^3\Pi_u$, $1^1\Pi_u$, $B^3\Sigma_u^-$, $c^1\Sigma_u^-$, and $1^1\Sigma_u^+$. Rates and cross section along the $1^1\Sigma_u^+$ dissociative route, leading to O(^{1}S) + O(^{1}D) atoms, have been published [Guberman and Giusti-Suzor, 1991] and

recent laser spectroscopy experiments [Lewis et al., 1995] have shown excellent agreement with our calculated $^1\Sigma_u^+$ potential curve and predissociation widths that we used to determine the DR cross sections and rates. For the $c^1\Sigma_u^-$ state, under NASA support, cross sections and rates have been calculated for the DR of the low ion vibrational levels. Because the c state crosses the ion near the inner turning point of v=4, its DR rate from v=0 is small, $4.6x10^{-11}cm^3/sec$ at 300K electron temperature, increasing to $2.9x10^{-9}cm^3/sec$ at 300K from v=4.

The $1^3\Pi_u$ potential curve, an important dissociative route leading to two ground state atoms, has been calculated at 28 internuclear distances in large CI calculations based on [5s,4p,3d,2f,1g] basis sets. These are state of the art calculations employing over two million configurations in the CI. The calculations take about 35 minutes at each internuclear distance on a Cray C90 supercomputer at the Pittsburgh Supercomputer Center.

Also under support of NASA grant NAGW-1404 we have enhanced the capabilities of the computer program which uses the multichannel quantum defect theory approach (MQDT) to calculate cross sections and rates. The program can now handle cases in which more than one dissociative route of the same electronic symmetry contributes to DR. The interaction between routes of the same symmetry can now be included in the calculation. In addition, the program can now handle more than one partial wave (angular momentum) for the free electron. For homonuclear diatomics, an accurate description of DR requires one or two partial waves, depending upon the molecule. For heteronuclear diatomics, often two or possibly three partial waves may be needed.

B. References

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D. Appendix

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